Description

METHOD FOR SIMULTANEOUS AND FRACTIONAL ANALYSIS

OF PERACETIC ACID AND HYDROGEN PEROXIDE

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Technical Field

The present invention relates to a method for fractional

determination of concentrations of peracetic acid and hydrogen

peroxide by measuring redox potentials in a reaction of a mixture

10   of peracetic acid and hydrogen peroxide with an iodide ion.

More specifically, it relates to a method for simultaneous and

fractional determination of concentrations of peracetic acid

and hydrogen peroxide by fractional measurement of redox

potentials in a reaction of a mixture of peracetic acid and

15   hydrogen peroxide with an iodide ion in a pH buffer solution

containing a molybdate, iodine and the iodide ion.

Background Art

Peracetic acid has found wide acceptance in medical and

20   food industries as a bactericide. Peracetic acid is by far

better in bactericidal activity than hydrogen peroxide which

has long been used as a bactericide. Further, peracetic acid

is by far lower in burden exerted on a material of a machine

and natural environment than sodium hypochlorite which has been

25   so far known as a bactericide. In foreign countries, especially

in the U. S. , peracetic acid has been often used as a bactericide to replace sodium hypochlorite. In recent years, peracetic acid has been used also in Japan as a bactericide, and its use amount has been rapidly increased year by year.

5   Since peracetic acid as a bactericide is usually synthesized from hydrogen peroxide and acetic acid, commercially available peracetic acid is a mixed aqueous solution of peracetic acid, hydrogen peroxide, acetic acid and the like. It is important to measure a concentration of

10   peracetic acid which is in the form of such a mixed aqueous solution. The concentration of peracetic acid is measured by a batchwise analytical method such as an iodine titration method (JP-A-6-130051), a spectroscopic method or a conductometric method (JP-T-6-503162 (the term "JP-T" as used herein means

15   a published Japanese translation of a PCT patent application), JP-UM-T-6-7057, JP-A-9-127053 and the like). In the batchwise analytical method, it is difficult to measure a concentration in situ instantaneously and continuously. In the ordinary conductometric method, total electroconductivity of a mixed

20   aqueous solution containing peracetic acid is examined, and it is therefore impossible to fractionally measure actual concentrations of peracetic acid, hydrogen peroxide and the like contained in a solution. Accordingly, the ordinary analytical methods are not satisfactory enough to measure

25   concentrations of peracetic acid, hydrogen peroxide and the

2

like exactly and adequately.

Accordingly, the invention aims to provide a method for fractionally measuring concentrations of peracetic acid and hydrogen peroxide in a mixture of peracetic acid and hydrogen

5   peroxide instantaneously, continuously and simultaneously using the fact that a reaction rate of peracetic acid with an iodide ion is different from a reaction rate of hydrogen peroxide with an iodide ion.

In a reaction of peracetic acid and an iodide ion and

10   a reaction of hydrogen peroxide and an iodide ion, the reaction rate is high in peracetic acid and low in hydrogen peroxide. However, there is a portion in which the reactions take place simultaneously. Thus, it is impossible to fractionally determine concentrations of peracetic acid and hydrogen

15   peroxide. Further, the reaction of hydrogen peroxide and the iodide ion is slow, and it takes much time to reach equilibrium. Accordingly, the reaction has been problematic when used in the analysis.

20   Disclosure of the Invention

For solving the foregoing problems, the present inventors have studied the reactivity of peracetic acid and hydrogen peroxide with the iodide ion in the presence of a molybdate, and have consequently found that in a specific pH range, a portion

25   in which a reaction of peracetic acid and an iodide ion and

a reaction of hydrogen peroxide and an iodide ion take place overlappingly is decreased and a reaction of hydrogen peroxide and an iodide ion reaches equilibrium in a relatively short time, and that redox potential changes in a reaction of peracetic

5   acid and an iodide ion and a reaction of hydrogen peroxide and an iodide ion are measured, whereby fractional determinations of the respective compounds can be performed in a short time. These findings have led to the completion of the invention.

That is, the invention is a method for simultaneous and

10 fractional determination of peracetic acid and hydrogen peroxide, which comprises adding a solution containing peracetic acid and hydrogen peroxide to a pH buffer solution with pH of from 5 to 6 containing a molybdate, iodine and an iodide ion, and measuring redox potential changes in a reaction

15 of peracetic acid and the iodide ion and a reaction of hydrogen peroxide and the iodide ion. Further, the invention is the method for simultaneous and fractional determination of peracetic acid and hydrogen peroxide, wherein the concentration of the molybdate is from 0.5 to 1 mmol/l, the concentration

20 of iodine is from 0.3 to 2 mmol/l, the concentration of the iodide ion is from 5 to 20 mmol/l, and redox potential changes are measured using a potentiometer having a working electrode made of platinum, gold or carbon.

25 Brief Description of the Drawings

4

Fig. 1 is an example of a cross-sectional drawing of a working electrode used in the invention. 1 is a working electrode, 2 a conductive metallic rod, 3 a conductive paste, 4 an electrode, and 5 a resin rod.

5   Fig. 2 is a graph showing a change with time of electrode potentials measured in Examples 1 and 2.

Fig. 3 is a graph in which an integrated value of an electrode potential change measured in Example 1 is plotted as a function of a concentration of peracetic acid (PAA) or

10   hydrogen peroxide (H_2O_2).

Best Mode for Carrying Out the Invention

The method for simultaneous and fractional determination of peracetic acid and hydrogen peroxide in the invention

15   comprises adding a solution containing peracetic acid and hydrogen peroxide to a predetermined pH buffer solution containing a molybdate, iodine and an iodide ion, and measuring redox potential changes (of the iodide ion and iodine) in a reaction of peracetic acid with the iodide ion and a reaction

20   of hydrogen peroxide with the iodide ion.

The invention is described in detail below.

In the invention, the pH of the pH buffer solution is from 5 to 6. When the pH is less than 5, peracetic acid and hydrogen peroxide are reacted with the iodide ion partially

25   overlappingly, which is disadvantageous to fractionally

determine peracetic acid and hydrogen peroxide. When the pH exceeds 6, it takes much time to reach equilibrium in the reaction of hydrogen peroxide with the iodide ion. When the pH is in the range of from 5 to 6, the portion in which the reactions take place overlappingly is decreased, and a time in which the reaction reaches equilibrium is relatively short, making it possible to perform fractional determination for a substantially short period of time. Incidentally, in the present specification, the fact that the portion in which the reaction of peracetic acid with the iodide ion and the reaction of hydrogen peroxide with the iodide ion take place overlappingly is decreased to enable the fractional determination indicates that selectivity is good, and the fact that the reactions take place partially overlappingly to make difficult the fractional determination indicates that selectivity is decreased.

The pH buffer solution with pH of from 5 to 6 may be formed by any method. However, since the reaction of peracetic acid or hydrogen peroxide with the iodide ion allows formation of acetic acid and water, an acetate buffer solution is preferable.

In the invention, the molybdate in the pH buffer solution acts as a catalyst for increasing the reaction rate of hydrogen peroxide and iodide ion. The reaction rate of hydrogen peroxide and the iodide ion is relatively low, and it takes time to reach equilibrium, and considerable time is required for determination. The addition of the molybdate to the pH buffer

6

solution increases the reaction rate of hydrogen peroxide and iodide ion to enable the measurement in a short period of time.

The molybdate used includes sodium molybdate, potassium molybdate, calcium molybdate and ammonium molybdate. In view

5 of stability in the solution, ammonium molybdate is preferable.

The concentration of the molybdate in the buffer solution is preferably from 0.5 to 1 mmol/l. In this range, the reaction of hydrogen peroxide with iodide ion is accelerated without hindrance of it, and the reaction of peracetic acid with iodide

10 ion is not hindered, nor is the reaction rate thereof influenced. When the concentration of the molybdate is less than 0.5 mmol/l, the reaction rate of hydrogen peroxide with iodide ion is not satisfactory. When it exceeds 1 mmol/l, the molybdate is hardly dissolved in the solution. In the invention, the unit mM of

15 the concentration indicates mmol/l unless otherwise instructed.

The molybdate may be added to the buffer solution from the beginning or after the completion of the reaction of peracetic acid during the analysis.

20 The ion source of the iodide ion used in the invention is not limited at all so long as it forms iodide ion in the pH buffer solution. Potassium iodide which is commonly used in iodometry is preferable because a high-purity compound can be available and is stable in the solution. The concentration

25 of the iodide ion is preferably from 5 to 20 mM. When the

7

concentration of the iodide ion is less than 5 mM, the redox potential in the initial concentration (before charging a sample) is not stable. When the concentration of the iodide ion exceeds 20 mM, the redox potential change becomes smaller

5   than the actual reaction amount of hydrogen peroxide or peracetic acid with iodide ion in some concentrations of hydrogen peroxide and peracetic acid in a sample to lower sensitivity and decrease selectivity.

The concentration of iodine in the buffer solution used

10   in the invention is preferably from 0.3 to 2 mM. When the concentration of iodine is less than 0.3 mM, the redox potential in the initial concentration (before charging a sample) is not stable. When the concentration of iodine exceeds 2 mM, the redox potential change becomes smaller than the actual reaction

15   amount of hydrogen peroxide or peracetic acid with iodide ion depending on the concentrations of hydrogen peroxide and peracetic acid in a sample to lower sensitivity and decrease selectivity.

A method for preparing a pH buffer solution with pH of

20   from 5 to 6 containing known concentrations of iodine and the iodide ion is not particularly limited so long as iodine and iodide ion in the buffer solution can be equilibrated. For example, an equilibrium solution of known concentrations of iodide ions and iodine can be prepared by dissolving a

25   predetermined amount of potassium iodide in a pH buffer solution

8

with pH from 5 to 6 and adding a known concentration of peracetic acid thereto to oxidize a part of iodide ions. Further, a fixed amount of iodine can be formed by dissolving a predetermined amount of potassium iodide in a pH buffer solution with pH of

5   from 5 to 6 and performing potentiostatic electrolysis while applying a known potential. Thus, an equilibrium solution of known concentrations of iodide ions and iodine can be prepared. Subsequently, a predetermined amount of a molybdate is added, and a pH buffer solution with pH from 5 to 6 containing a molybdate

10   and known concentrations of iodine and iodide ions can be prepared.

A working electrode, a platinum wire as a counter electrode and Ag/AgCl (NaCl saturation) as a reference electrode are dipped in the pH buffer solution with pH from 5 to 6 containing a molybdate

15   and known concentrations of iodine and an iodide ion, which is prepared by the foregoing method. A sample solution containing peracetic acid and hydrogen peroxide is added thereto to measure electrode potentials. Concentrations of peracetic acid and hydrogen peroxide are estimated from the electrode

20   potential change (redox potential change) using calibration curves previously obtained. A glassy carbon electrode, a platinum electrode or a gold electrode prepared in Example 1 as shown in Fig. 1 is preferably used as an example of the working electrode. It is preferable that the measurement is conducted

25   under stirring with a stirring unit such as a stirrer bar for

uniformly conducting a redox reaction. It may be conducted in a nitrogen atmosphere or in an air atmosphere.

With respect to the measurement of the redox potential in the invention, a working electrode and a reference electrode

5   such as a silver/silver chloride (potassium chloride saturated solution) or calomel electrode having a known standard potential are set in a measuring solution, and a potential of the working electrode relative to the reference electrode is measured with a potentiostat or an electrometer. A redox potential can also

10   be measured by a potential measuring device of a three-electrode system having a working electrode, a counter electrode and a reference electrode. Regarding measurement precision of a potential measuring device, it is advisable that a potential of 100 μV, preferably a potential of 10 μV can be detected.

15   Fig. 2 shows a change with time of electrode potentials (redox potentials) measured at room temperature (25°C ± 1°C) at times (1), (2), (3), (4), (5), (6), (7), (8), (9) and (10) by addition of a sample solution containing different known concentrations of peracetic acid and hydrogen peroxide.

20   Immediately after the addition of the sample solution, the instantaneous electrode potential change depending on the fast reaction of the iodide ion and peracetic acid and the moderate electrode potential change depending on the subsequent reaction of iodide ion and hydrogen peroxide are obtained.

25   The integrated value (ΔE_1) of each electrode potential

10

change (ΔE) is plotted as a function of the concentration of peracetic acid or hydrogen peroxide according to theoretical formula (1) (Fig. 3). Each plot is then linear, and the slope thereof nearly agrees with a theoretically expected value (29.6 mV at 25°C). In this manner, the concentrations of peracetic acid and hydrogen peroxide can be determined by measuring the electrode potentials depending on the reaction of peracetic acid with the iodide ion and the reaction of hydrogen peroxide with the iodide ion using the buffer solution with the known iodine concentration and the known iodide ion concentration. Theoretical formula (1)

$$\Delta E=(2.303RT/2F)\log\{(1+[Ox]/[I_2]_0)/(1-2[Ox]/[I^-]_0)^2\} \quad (1)$$

wherein ΔE represents a potential change (mV), R represents a gas constant, F represents a Faraday constant, T represents a measuring temperature (absolute temperature), [Ox] represents a concentration (M) of peracetic acid or hydrogen peroxide, and $[I^-]_0$ and $[I_2]_0$ represent initial concentrations (M) of an iodide ion and iodine.

According to the method of the invention, the concentrations of peracetic acid and hydrogen peroxide in the mixed solution of peracetic acid at a concentration of from 5 μM to 4.5 mM and hydrogen peroxide at a concentration of from 2 μM to 1.3 mM can fractionally be measured with good accuracy.

Examples

11

The invention is illustrated more specifically below by

referring to Examples.

Example 1

[Preparation of an acetate buffer solution containing an iodide

5   ion and iodine]

To a glass cell having a volume of 80 cc, 40 cc of a 0.05

M acetate buffer solution (pH 5.4) is charged, and potassium

iodide is dissolved therein to a concentration of 13.5 mM.

Subsequently, a mixed solution of peracetic acid and hydrogen

10   peroxide is added such that the total concentration becomes

1.0 mM to oxidize the iodide ion and form 1.0 mM of iodine.

The iodide ion concentration of the thus-obtained acetate buffer

solution is 11.5 mM (13.5-2x1.0).

[Production of a working electrode]

15   As shown in Fig. 1, a conductive metallic rod (copper

rod) 2 having a diameter of 2 mm as a conductive substrate,

a glassy carbon (or, platinum or gold) electrode 4 having a

diameter of 3 mm and a length of 4 mm and a polyimide resin

rod 5 were embedded such that the surfaces of the conductive

20   metallic rod 2 and the glassy carbon electrode 4 and one end

of the polyimide resin rod 5 were situated on approximately

the same plane and the conductive metallic rod 2 was exposed

from another surface of the polyimide resin 5 by approximately

5 cm.   The exposed surface of the glassy carbon (or, platinum

25   or gold) was polished with an alumina powder having a diameter

12

of 1.0 μm and an alumina powder having a diameter of 0.06 μm,

and then put in distilled water to conduct ultrasonic cleaning

for 3 minutes. In this manner, the glassy carbon electrode

(referred to as a working electrode (A)), the platinum electrode

5   (referred to as a working electrode (B)) and the gold electrode

(referred to as a working electrode (C)) were produced. The

working electrodes (B) and (C) were further electrolyzed by

potential sweeping in a 0.05 M sulfuric acid aqueous solution

at a potential of from -0.2 to 1.5 V with 10 Vs^{-1} relative to

10   an Ag/AgCl (NaCl-saturated) reference electrode, and then used

as working electrodes.

[Method for measuring a potential]

A working electrode, a platinum wire (diameter 1 mm, length

10 cm) as a counter electrode and an Ag/AgCl (NaCl-saturated)

15   reference electrode were dipped in the above-prepared acetate

buffer solution, and dissolved oxygen was removed through a

nitrogen gas. Then, an electrode potential of the working

electrode was measured relative to the reference electrode using

a potentiostat as a three-electrode electrolysis system. The

20   measurement was conducted at room temperature (25°C ± 1°C) under

stirring with a stirrer bar. For accelerating a reaction of

an iodide ion with hydrogen peroxide, ammonium molybdate was

added to a concentration of 0.8 mM.

Peracetic acid and hydrogen peroxide were added at (1),

25   (2), (3), (4), (5), (6), (7), (8), (9) and (10) so as to give

13

respective mixed solutions in which the concentrations of

peracetic acid (PAA) and hydrogen peroxide (H_2O_2) were 0.275

mM and 0.085 mM, 0.55 mM and 0.17 mM, 0.825 mM and 0.25 mM,

1.10 mM and 0.34 mM, 1.375 mM and 0.42 mM, 1.65 mM and 0.50

5   mM, 1.92 mM and 0.59 mM, 2.20 mM and 0.68 mM, 2.47 mM and 0.76

mM, and 2.75 mM and 0.85 mM. The electrode potential change

with time obtained using the working electrode (A) is shown

in Fig. 2. In any of these cases, the instantaneous electrode

potential change depending on the fast reaction of the iodide

10   ion with peracetic acid and the moderate electrode potential

change depending on the subsequent reaction of the iodide ion

with hydrogen peroxide were obtained by the addition of the

mixed solution of peracetic acid and hydrogen peroxide. An

integrated value (ΔE_1) of a potential change (ΔE) at this time

15   is plotted in the ordinate as a function of a concentration

of peracetic acid or hydrogen peroxide according to the

theoretical   formula   (1),   and

$\log\{(1+[Ox]/[I_2]_0)/(1-2[Ox]/[I^-]_0)^2\}$ is plotted in the abscissa.

The results are shown in Fig. 3.

20   Theoretical formula (1)

$\Delta E=(2.303RT/2F)\log\{(1+[Ox]/[I_2]_0)/(1-2[Ox]/[I^-]_0)^2\}$ (1)

wherein ΔE represents a potential change (mV), R represents

a gas constant, F represents a Faraday constant, T represents

a   measuring   temperature   (absolute   temperature),   [Ox]

25   represents a concentration (M) of peracetic acid or hydrogen

peroxide, and $[I^-]_0$ and $[I_2]_0$ represent initial concentrations (M) of an iodide ion and iodine.

The plot is linear, and the slope thereof is found to be 29.3 mV for peracetic acid and 30.5 mV for hydrogen peroxide, and these nearly agree with a theoretically expected value (29.6 mV at 25°C). Thus, the concentrations of peracetic acid and hydrogen peroxide can be determined by measuring electrode potential changes depending on peracetic acid and hydrogen peroxide using the acetate buffer solution in which $[I^2]_0$ and $[I^-]_0$ are known.

Example 2

Example 1 was repeated except that dissolved oxygen was not removed through a nitrogen gas and the measurement was conducted in an acetate buffer solution under air saturation. The results of measurement are shown in Fig. 2. The plot is linear, and the slope thereof is shown in Table 1. This measuring method is not influenced by oxygen.

Example 3

The measurement was conducted as in Examples 1 and 2 except that the working electrode (B) was used. The results of measurement are shown in Table 1. The plot is linear, and the slope value thereof nearly agrees with the theoretical value. The concentrations of peracetic acid and hydrogen peroxide can be determined simultaneously by this measuring method in a nitrogen atmosphere and in an air atmosphere using a platinum

15

electrode.

Example 4

The measurement was conducted as in Examples 1 and 2 except that the working electrode(C) was used. The results of measurement are shown in Table 1. The plot is linear, and the slope value thereof nearly agrees with the theoretical value. The concentrations of peracetic acid and hydrogen peroxide can be determined simultaneously by this measuring method in a nitrogen atmosphere and in an air atmosphere using a gold electrode.

Table 1

		Slope (mV)			
	Electrode	Peracetic acid		Hydrogen peroxide	
		in a nitrogen atmosphere	in an air atmosphere	in a nitrogen atmosphere	in an air atmosphere
Ex. 1	Glassy carbon	29.3		30.5	
Ex. 2	Glassy carbon		31.8		32.5
Ex. 3	Platinum	32.3	31.1	27.9	32.0
Ex. 4	Gold	31.9	32.0	31.0	32.0

Example 5

[Preparation of an acetate buffer solution containing an iodide ion and iodine]

To a glass cell having a volume of 80 cc, 40 cc of a 0.05 M acetate buffer solution (pH 5.4) is charged, and potassium iodide is dissolved therein to a concentration of 11.5 mM.

16

Subsequently, potentiostatic electrolysis is performed using a platinum electrode (area 1 cm^2) as a working electrode, a platinum wire as a counter electrode and an Ag/AgCl (NaCl-saturated) electrode as a reference electrode while

5   applying a potential of 1.2 V to the working electrode, whereby an iodide ion is electrolytically oxidized to generate 1.5 mM iodine. The iodide ion concentration of the thus-obtained acetate buffer solution is 8.5 mM (11.5-2x1.5).

[Method for measuring a potential]

10   A working electrode (A), a platinum wire as a counter electrode and an Ag/AgCl (NaCl-saturated) reference electrode were dipped in the above-prepared acetate buffer solution, and dissolved oxygen was removed through a nitrogen gas. Then, an electrode potential of the working electrode (A) was measured

15   relative to the reference electrode using a potentiostat manufactured by ALS/CHI as a three-electrode electrolysis system. The measurement was conducted at room temperature (25°C ± 1°C) under stirring with a stirrer bar. For accelerating a reaction of an iodide ion with hydrogen peroxide, ammonium

20   molybdate was added to a concentration of 0.8 mM.

Peracetic acid and hydrogen peroxide were added so as to give respective mixed solutions in which the concentrations of peracetic acid and hydrogen peroxide were 0.687 mM and 0.222 mM, 1.375 mM and 0.444 mM, 2.06 mM and 0.666 mM, and 2.75 mM

25   and 0.889 mM. In any of these cases, the instantaneous electrode

17

potential change depending on the fast reaction of the iodide

ion with peracetic acid and the moderate electrode potential

change depending on the subsequent reaction of the iodide ion

with hydrogen peroxide were obtained by the addition of the

5 mixed solution of peracetic acid and hydrogen peroxide. An

integrated value (ΔE_1) of a potential change (ΔE) at this time

is plotted in the ordinate as a function of a concentration

of peracetic acid or hydrogen peroxide according to the

theoretical   formula   (1),   and

10 $\log\{(1+[Ox]/I_2)_0\}/(1-2[Ox]/[I^-]_0)^2\}$ is plotted in the abscissa.

Then, the plot is linear, and the slope thereof is found to

be 29.1 mV for peracetic acid and 29.3 mV for hydrogen peroxide,

and these nearly agree with a theoretically expected value (29.6

mV at 25°C). Thus, the concentrations of peracetic acid and

15 hydrogen peroxide in the mixed solution of peracetic acid and

hydrogen peroxide can be determined simultaneously by this

method.

Industrial Applicability

20   According to the invention, the concentrations of

peracetic acid and hydrogen peroxide in the mixture of peracetic

acid and hydrogen peroxide can fractionally be measured with

ease continuously and simultaneously.

18